Effects of Magnetization on Hole Localization and MnO$_6$ Octahedra Disorder in Hole-Doped Lanthanum Manganese Perovskites

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Abstract

We review the distortions of the MnO$_6$ octahedra reduced by magnetization in hole-doped lanthanum manganese perovskites. The systems we consider include the "colossal" magnetoresistance (CMR) samples La$_{1-x}$Ca$_x$MnO$_3$ (x=0.21, 0.25, 0.30), La$_{0.67}$Ba$_{0.33}$MnO$_3$, and a poorer quality La$_{0.67}$Pb$_{0.33}$MnO$_3$ sample. We also report preliminary work on three samples of oxygen-doped LaMnO$_{3+\delta}$ and a lanthanum-deficient La$_{0.9}$MnO$_3$ sample. We find the same exponential relationship between the removal of the distortion and the sample magnetization in the Ba- and Pb-doped CMR samples as was found previously for the Ca doped samples. The MnO$_6$ distortion in the oxygen-doped materials is found to slightly reduce below the magnetic transition, although much less so than in the CMR samples. Above T_C, the antiferromagnetic LaMnO$_{3.006}$ sample shows a softer temperature dependence of the Mn-O bond length distribution broadening. Surprisingly, even this sample shows deviations from thermal (Debye) behavior near T_N, possibly due to FM coupling within MnO planes.

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1. Introduction

The so-called "colossal" magnetoresistance materials [1] have proven to have the largest spin-charge-lattice coupling of any material measured to date. Local structure studies that focus on the MnO_6 octahedra distortions have proven to be effective probes for studying the lattice coupling. The $La_{1-x}Ca_xMnO_3$ is a good one to consider because the end-member compounds $LaMnO_3$ and $CaMnO_3$ exist, and therefore trends from $x=0-1$ can be observed. The fundamental electronic difference between the end compounds is that Mn is 3+ in $LaMnO_3$ and Mn is 4+ in $CaMnO_3$. Structurally, these compounds are nearly identical, except for lattice parameter changes and a Jahn-Teller (JT) distortion that occurs around the Mn^{3+} ions. These compounds are also similar magnetically, with each being antiferromagnetic (AF) near 130 K. However, the AF state in $LaMnO_3$ is very sensitive to hole doping: for mean Mn valence < 3.5 the samples are typically ferromagnetic (FM). In the high temperature paramagnetic state for the Ca [2] and Sr [3] doped systems, the local structure can be thought of as a linear combination of JT-distorted MnO_6 octahedra around Mn^{3+} sites, and well-ordered octahedra around Mn^{4+} sites. The dramatic spin-lattice coupling was first demonstrated in a pair-distribution function (PDF) analysis of diffraction data [4]. This study found that the large distortion of the octahedra was drastically reduced below the FM transition. However, another PDF study [3] and x-ray-absorption fine-structure (XAFS) experiments [5] found that the distortion, while very much reduced, was still present. Recently, we found a simple relationship between the reduction of the distortion and the sample magnetization in CMR samples of $La_{1-x}Ca_xMnO_3$, demonstrating that this residual distortion is probably due to unsaturated magnetic moments [2].

The purpose of this study is to consider the effects of magnetization on other hole-doped lanthanum-manganite perovskites. We report on the functional dependence of the MnO_6 distortion with magnetization for two other CMR materials, $La_{0.67}Ba_{0.33}MnO_3$ and $La_{0.67}Pb_{0.33}MnO_3$, and report data on samples with excess-oxygen and lanthanum-deficient $LaMnO_3$. We use the XAFS technique to focus on the Mn-O bonds in the MnO_6 octahedra environment.

Sample preparation details for the Ba and Pb doped samples are in Ref. [5], except that BaO was used instead of PbO for the Ba-doped sample. The Ba-doped sample has a ferromagnetic transition at ~330 K (T_C from peak in derivative). The Pb-doped sample has a T_C~250 K, which

is much lower than the usual value for high quality samples (above 300 K). Preparation of the $La_{1-y}MnO_{3+\delta}$ samples will be presented in a future paper. Samples of $LaMnO_{3.07}$, $LaMnO_{3.10}$, and $La_{0.9}MnO_3$ were titrated to determine the mean Mn valence. These samples all show a FM transition, and $La_{0.9}MnO_3$ has nearly the full moment at low temperatures. The oxygen content for an AF sample of $LaMnO_{3.006}$ was determined by thermal gravimetric analysis.

2. CMR samples and functional relation between distortions and magnetization

The CMR samples show the largest structural effects, so we will begin our discussion with them. Data quality and reduction procedures have been reported earlier [5,6]. Here we only report the effect of removing the polaron distortion in the FM state. This procedure is discussed in Ref. [2,6], but essentially consists of fitting a Debye curve to the width of the Mn-O bond length distribution in the paramagnetic state as a function of temperature (σ_T^2), extending this fitted curve to below the FM transition and subtracting the data from it. The Debye fit must include the static contribution of the full polaron distortion (σ_{FP}^2), and the subtraction is done in quadrature:

$$\Delta\sigma^2 = (\sigma_T^2 + \sigma_{FP}^2) - \sigma_{data}^2.$$

The resulting $\Delta\sigma^2$ is the change in the bond length distribution width with the mundane Debye contribution approximately removed. This quantity should be directly correlated with the magnetization if double exchange induces lattice distortions in these materials [7]. Figure 1 shows $\ln(\Delta\sigma^2)$ as a function of the reduced magnetization for $La_{0.67}Ba_{0.33}MnO_3$ and $La_{0.67}Pb_{0.33}MnO_3$. We find that these data fall on a straight line, as we found earlier [2,6] for calcium doped CMR samples (shown in Fig. 1 for comparison). Note that the slope of the Ba line is roughly the same as for the calcium data. The Pb data, on the other hand, has a larger slope. This may be a consequence of the low quality of this sample, as indicated by the low T_C. These data are consistent with a simple model whereby each doped hole is either localized (causing a polaron distortion) or delocalized (causing no polaron distortion) [2]. Within this model the delocalized hole concentration n_{dh} changes as $\ln(n_{dh}) \propto M$. This result is in agreement with the dependence of the resistivity on magnetization $\ln(\rho) \propto -M$ [8].

3. Effect of hole-doping in off-stoichiometric $La_{1-y}MnO_{3+\delta}$

Next we consider the effect of hole doping with excess oxygen or deficient lanthanum. The magnetization data for these materials are reported in Fig. 2. Only the $La_{0.9}MnO_3$ sample is truly ferromagnetic. The other samples have severely reduced moments, and the $LaMnO_{3.006}$ sample is AF. In order to extract the near neighbor Mn-O bond length distribution width σ from our data, we will have to perform fits as used for Fig. 1. However, at this time we have not obtained sufficiently high quality fits. For this study, we report the amplitude of the first peak in the Fourier transform of the XAFS function $k\chi(k)$. The amplitude of this peak depends on several factors that will remain nearly constant between the different samples, and also is proportional to $1/\sigma$ (assuming a Gaussian distribution, which is only approximately true for a JT distortion). These amplitudes are displayed in Fig. 3.

There are several interesting features in the data in Fig. 3. If we only look at the data above the magnetic transitions (marked by arrows), one notices that the FT peak amplitude decreases somewhat more quickly for the $LaMnO_{3.006}$ sample than for the others. It is possible that the presence of holes in the lattice (which are nearly non-existent in the $LaMnO_{3.006}$ sample) constrain the JT distortions around the Mn^{3+} ions to create a stiffer overall Mn-O bond environment. In any case, the correlated-Debye temperature Θ_D is estimated to be ~ 600 K for this sample in the paramagnetic state. The other $LaMnO_3$ samples are consistent with Θ_D~850 K, which is consistent with the paramagnetic state in the rest of the $La_{1-x}Ca_xMnO_3$ series [6].

Since the presence of holes and ferromagnetism allows double-exchange hopping to occur, we expect to see some ordering of the MnO_6 octahedra at T_C. Surprisingly, we also see an ordering at T_N in the AF $LaMnO_{3.006}$ sample. We speculate that the increased ordering at the AF transition comes from the FM coupling within MnO planes [9]. Of course, the ordering measured here is very much smaller than occurs in CMR samples. In these non-CMR samples, the decrease in the bond length distribution width σ is only ~6-8%. In CMR samples, the decrease in σ is on the order of 20%. Such ordering in the magnitude occurs in $La_{0.9}MnO_3$ (Fig. 4). Although magnetoresistance data has not yet been obtained for this sample, it is almost certainly CMR.

To conclude, we have demonstrated that the dependence of the polaron distortion on the magnetization $\ln(\Delta\sigma^2) \propto -M$ previously measured for Ca-doped CMR manganites also holds for Ba- and Pb-doped manganites. The effect of hole-doping with excess oxygen has been considered, and clear changes at T_C are observed for the MnO_6 octahedral ordering, although not nearly as large as for the CMR samples. A sample of $La_{0.9}MnO_3$ was also measured, which displayed a sharp bond ordering of the octahedra at T_C, strongly suggesting that this is indeed a CMR sample.

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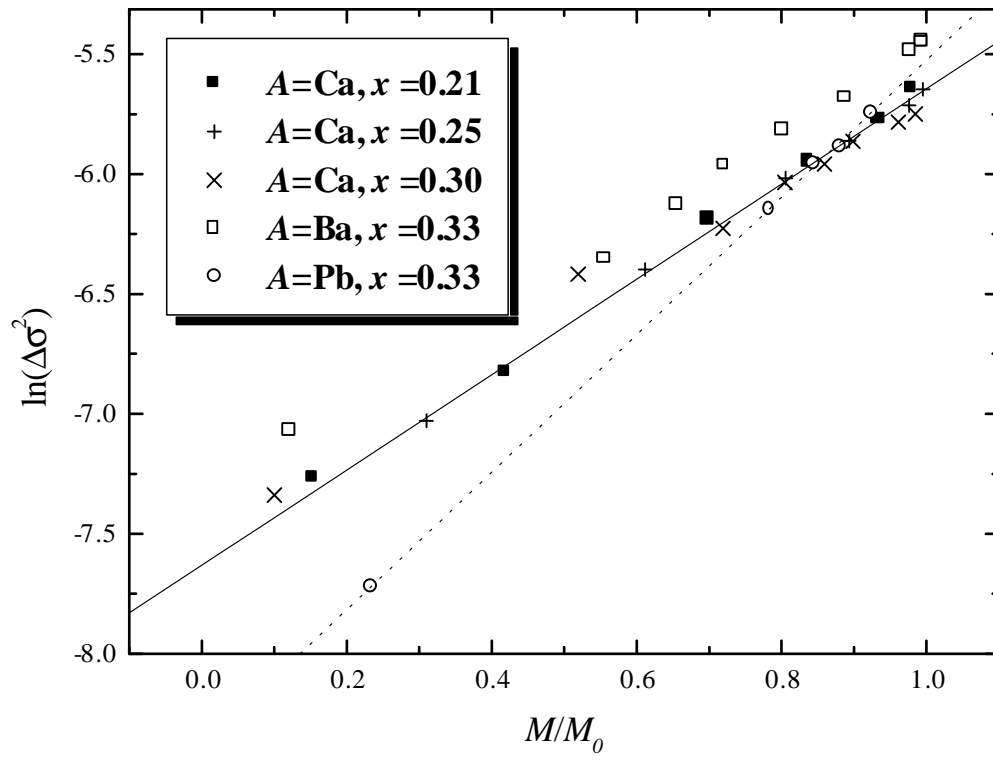9. E. O. Wollan and W. C. Koehler, Phys. Rev. **100**, 545 (1955).

Figure Captions:

Fig. 1: $\ln(\Delta\sigma^2)$ vs. M/M_0 for samples of La$_{1-x}$A$_x$MnO$_3$, where $\Delta\sigma^2$ is the amount of distortion in the Mn-O bond length distribution removed by the magnetization M, which is normalized by the low-temperature magnetization M_0.
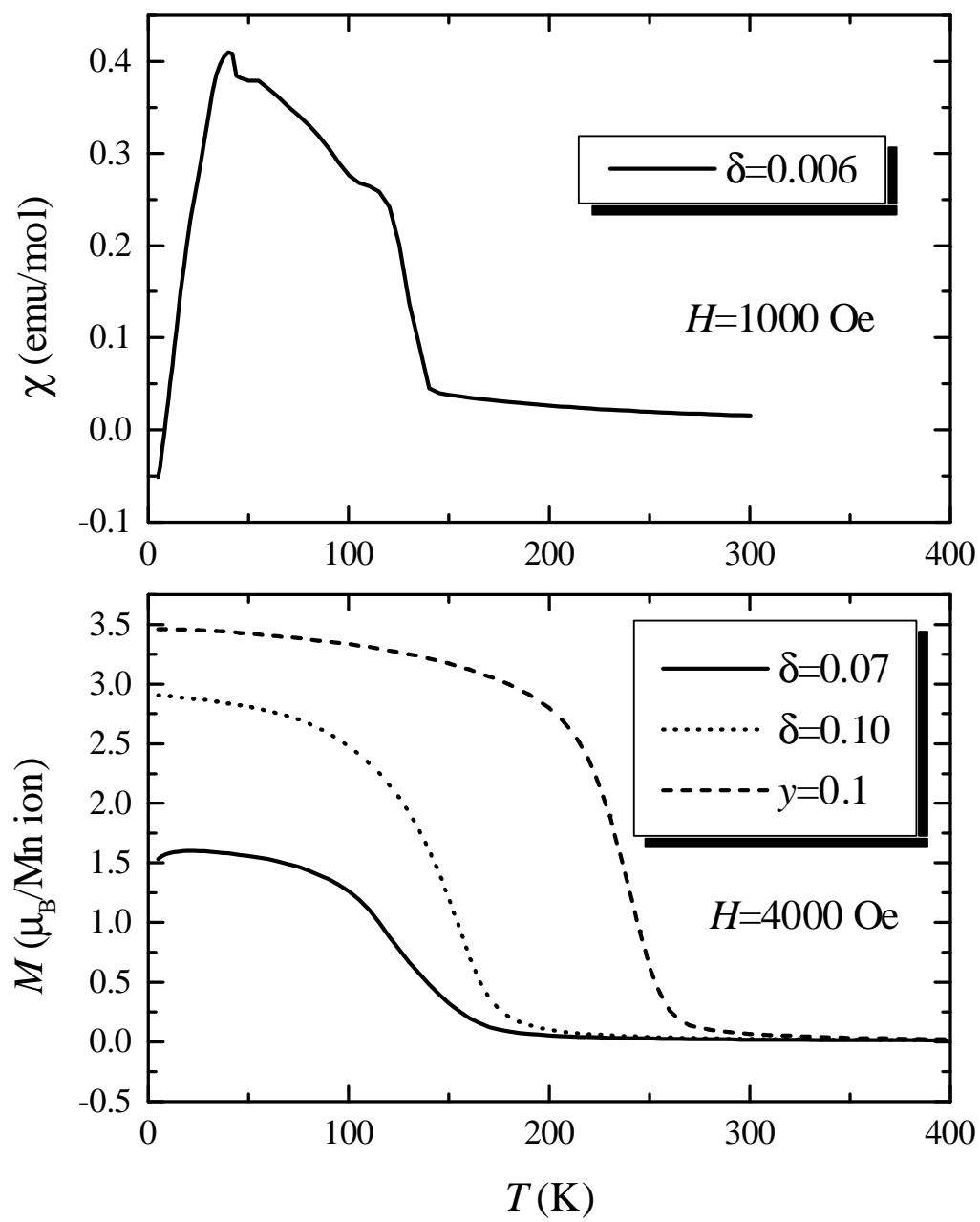
Fig. 2: The upper panel shows susceptibility $\chi(T)$ for the antiferromagnetic LaMnO$_{3.006}$ sample. The lower panel shows the magnetization curves for LaMnO$_{3.07}$, LaMnO$_{3.10}$ and La$_{0.9}$MnO$_3$.

Fig. 3. Amplitude of the near-neighbor Mn-O peak in the Fourier transform of $k\chi(k)$ for the oxygen-excess LaMnO$_{3+\delta}$ samples. Dotted lines are only guides to the eye. This amplitude is proportional to $1/\sigma$. Solid lines are approximate fits to a correlated-Debye model above the magnetic transitions, which are indicated with arrows. Data and fit for $\delta=0.10$ are offset by 0.03 for clarity.

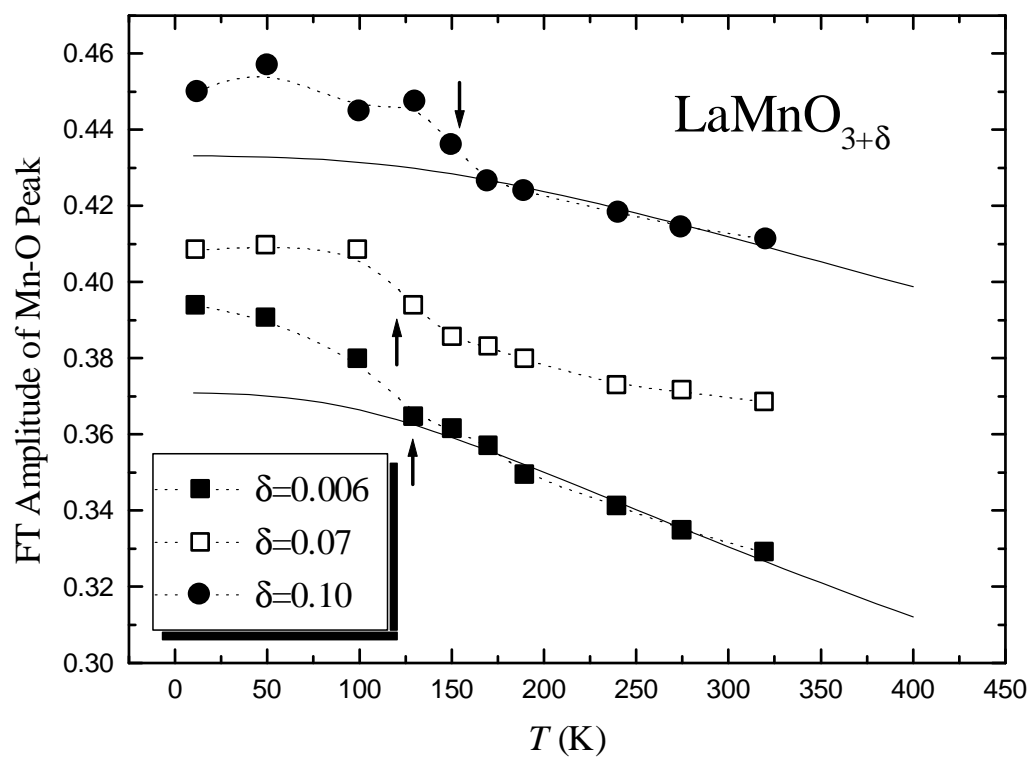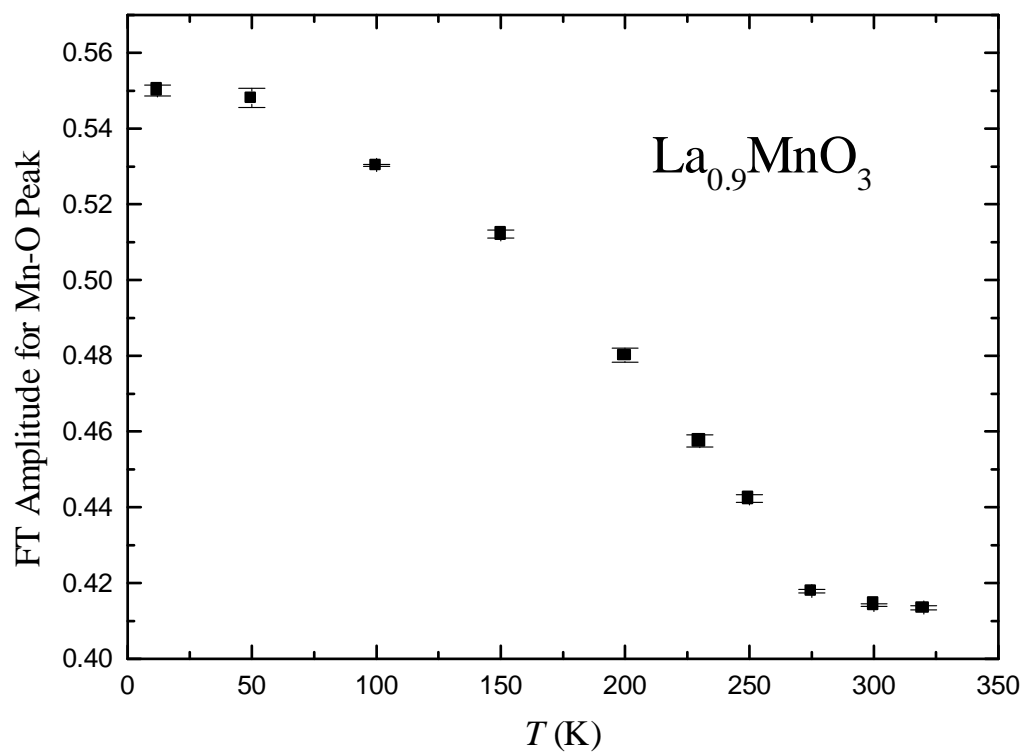Fig. 4. Amplitude of the near-neighbor Mn-O peak in the Fourier transform of $k\chi(k)$ for lanthanum deficient La$_{0.9}$MnO$_3$.

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Fig. 2

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Fig. 4